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(54) Title: **NANO COMPOSITE MATERIALS WITH ENHANCED PROPERTIES**

(57) Abstract: The present invention relates to a nano dispersion comprising a layered clay and a compound intercalated within the gallery regions of said clay, characterised in that said compound contains one or more hydrophilic terminal groups; nano composite materials formulated; the process for production of nano composite materials using said nano dispersion and the enhancement of the properties of the nano composite materials produced.



**WO 03/059817 A2**

Nano composite materials with enhanced properties

## 5 Field of the Invention

The present invention relates to nanodispersions and to nano composite materials formulated therewith including processes for their production and their use in different applications.

10

## Background of the Invention.

15 Polymers are widely employed in many areas of technology. The market for polymers with different or enhanced properties is growing owing to the demand for improvements on existing polymers and the search for new applications. Recently there has been considerable interest in forming composite materials consisting of a polymer matrix having an exfoliated layered material dispersed in the polymer matrix.

20 One approach to forming such composites involves polymerizing a monomer in the presence of layered material pre-treated with a swelling agent (see U.S. Pat. No. 4,810,734 and U.S. Pat. No. 4,889,885).

25 In PCT published application WO 93/04118 a process is disclosed for forming a polymeric nanocomposites using a melt-processible polymer and a swellable and polymer compatible intercalated layer material.

30 In U.S. Pat. No. 5,552,469 an intercalate capable of being exfoliated in a polymer matrix is disclosed. The intercalate consists of a layered material swelled by water and a water soluble polymer.

U.S. Pat. No. 5,576,372 and U.S. Pat. No. 5,576,373 disclose a nanocomposite comprising a rubber which has a positively charged group, and a layered silicate that has a negative charge on the silicate whereby the negative charge on the silicate is connected to the

positive charge on the reactive rubber through ionic bonding or association thereby overcoming the bonding force between the layers of the silicate resulting in their separation.

5 U.S. Pat. No. 4,889,885 discloses nanocomposites comprising certain resins and a layered silicate dispersed therein, said layered silicate having a layer thickness of 7-12 .ANG. and an interlayer distance of 30 .ANG. or above. Based on the x-ray diffraction data the compositions are entirely exfoliated.

10 Notwithstanding the foregoing, there is a continuous need for practical application of nanocomposite materials and effective incorporation of layered minerals in a polymer matrix in such a way as to provide an end material with improved properties.

In particular, it is an object of the present invention to provide new polymers having  
15 enhanced properties, which are particularly suitable for processing utilising the conventional techniques of manufacture of existing polymers.

Another object of the present invention is to provide polymers, which can be processed utilising cost effective means, i.e. the manufacture of these polymers without the need for  
20 costly additives such as solvents or costly solvent recovery and / or downstream processing.

A further object of the present invention is to provide thermoplastic polymers with enhanced modulus, strength, softening point, abrasion resistance, hardness, and melt  
25 rheology.

Another object of the present invention is to provide thermosetting polymers with enhanced modulus, abrasion resistance, hardness, and strength

30 Another object of the present invention is to provide elastomers with the enhanced properties of thermoplastic and thermosetting polymers.

Another object of the present invention is to provide polymer films with enhanced abrasion resistance, hardness, barrier properties, and water / solvent resistance.

5 A further object of the present invention is to provide foams with enhanced elastic modulus, tensile strength, tensile modulus, and compression strength.

A still further object of the present invention is to provide polymers with enhanced barrier properties, water / solvent resistance, thermal / UV ageing resistance and fire resistance.

10 Further objects, aspects and enhancements of this invention will become apparent upon reviewing the following description and appended claims.

It has now been surprisingly found that polymers formulated on the basis of specific nano dispersions address the aforementioned need. According to the present invention, specific  
15 nano composite materials are produced using a nano dispersion comprising a layered clay and a specific compound intercalated within the gallery regions of said clay, characterised in that said compound contains one or more hydrophilic terminal groups.

It has been surprisingly found that the intercalating compound according to the present  
20 invention allows the tailoring of the state or morphology of nano dispersion with respect to the nano composite materials formulated therewith.

Nano composite materials are known in the art, for example patent numbers WO 99/42518, WO 99/07790, U.S. 5,866,645, U.S. 5,853,866, WO 99/32403 and WO 00/47657.  
25 Nanocomposite materials filler are known to exhibit properties which are superior to those of the individual components. For optimisation of these properties, it is usually desirable to disperse the inorganic material on a nanometer length scale (Giannelis, E. P. JOM 44 28 (1992); Gleiter, H. Adv Mater. 4 474 (1992); and Novak, B. M., Adv. Mater. 5 422 (1993)). Nano composite materials exhibit many enhanced physical properties at a much  
30 lower volume percent of filler than conventional filled polymers.

However, none of the prior art documents suggest the key nature of this compound for use with the specific nano composite materials within the scope of the present invention,

neither do they disclose the presently claimed compositions or the benefits associated therewith.

## Detailed Description of the Invention

5

### Definitions

Within the scope of this patent the terms below are deemed to have following meanings:

10 “Nano dispersion” shall mean that the clay is substantially an intercalate and / or an exfoliate and is dispersed in the compound. [constituents of the polymeric matrix]

“Nano composite material” shall mean that the clay is substantially an intercalate and / or an exfoliate and is dispersed in the polymeric matrix. [cured polymer]

15

“Layered clay” shall mean an inorganic material such as a smectite clay, that is in the form of a plurality of adjacent and bound layers.

20 “Platelets” shall mean individual layers of a clay. “Gallery spacing”, denoted “d”, is the sum of the platelet thickness and the distance between adjacent alligned platelets.

“Tactoids” shall mean a plurality of stacked platelets

25 “Intercalation” shall mean the process of forming an intercalate by sorption of a suitable compound within the gallery regions of a layered clay.

“Intercalate” shall mean a product of an intercalation step, a layered clay having a compound sorbed within its gallery regions.

30 “Intercalated” shall mean a compound positioned within the gallery regions of a layered clay.

“Co-intercalation” shall mean the process of forming an intercalate by sorption of a second or plurality of suitable compounds within the gallery regions of the layered clay.

5 “Exfoliate” shall mean the product of an exfoliation step, the galleries of the intercalate are sufficiently disordered such that no ‘d’ spacing related peaks of the clay were discerned through WAXS (wide angle x-ray scattering) and SAXS (small angle x-ray scattering).

10 “Exfoliated” shall mean that the galleries of the intercalate are sufficiently disordered such that no ‘d’ spacing related peaks of the clay were discerned through WAXS (wide angle x-ray scattering) and SAXS (small angle x-ray scattering).

“Exfoliation” shall mean a process for forming an exfoliate from an intercalate.

15 The present invention is directed to nanodispersions, in particular the present invention is directed to intercalated layered materials prepared by contacting, and thereby intercalating, a layered silicate material, e.g., a phyllosilicate, such as a smectite clay, with a compound, characterised in that said compound contains one or more hydrophilic terminal groups (hereinafter referred to as intercalating compound)

20 Preferably the intercalating compound is characterized in having a hydrophobic unit (B) tipped with hydrophilic units (A).

25 In another embodiment, the present invention is directed to said nanodispersions further comprising an isocyanate reactive compound which optionally may be co-intercalated (as co-intercalant polymerizable reactants, or as the oligomer co-intercalant or polymer co-intercalant) to form nanocomposite materials. Preferred co-intercalants are polyols.

30 To form the intercalated and exfoliated materials of the present invention, the layered material, e.g., the phyllosilicate, should be swelled or intercalated by sorption of the intercalating compound to form the nanodispersion of the present invention. To form the co-intercalated materials of the preferred embodiment of the present invention, the compound-intercalated layered material is co-intercalated with said isocyanate reactive

compound optionally with additives such as catalyst, chain extenders, viscosity modifier and the like.

Nanocomposite material :

5

In a preferred embodiment of the present invention, the nanodispersion can be dispersed in a matrix monomer followed by polymerization of the matrix monomer, in-situ, e.g., by adding a curing agent, to form the nanocomposite material. The curing agents are then co-intercalated between platelets of the compound-intercalated clay followed by  
10 polymerization of the curing agent and the compound that have been intercalated into the clay interlayer galleries.

The curing agent for the polymer matrix is chosen for its ability to cure specific nano dispersions and therefore tailor the particular nano composite material desired. In a  
15 preferred embodiment of the present invention, the curing agent is a polyisocyanate composition. Accordingly, the nano composite materials formed thereof are polyurethanes. The term "polyisocyanate composition" in the present patent application is to be construed as including prepolymer and free polyisocyanate.

20 Organic polyisocyanates which may be used in the preparation of the polyisocyanate compositions of the invention include aliphatic, cycloaliphatic and araliphatic polyisocyanates, for example hexamethylene diisocyanate, isophorone diisocyanate, cyclohexane-1,4-diisocyanate, dicyclo-hexylmethane-4,4-diisocyanate an p-xylylene diisocyanate.

25

Preferred co-intercalated materials which may be used alone or in admixture are diisocyanates such as 1,5-naphthalene diisocyanate; p-phenylene diisocyanate, m-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4'-diphenylmethane diisocyanate, 3,3'-dimethyl-4,4'-  
30 biphenyl diisocyanate, 4,4'-diphenylisopropylidene diisocyanate, 3,3'-dimethyl-4,4'-diphenyl diisocyanate, 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, 3,3'-dimethoxy-4,4'-biphenyl diisocyanate, dianisidine diisocyanate, toluidine diisocyanate, hexamethylene diisocyanate, 4,4'-diisocyanatodiphenylmethane and the like or mixtures thereof.

The highly preferred polyisocyanates are the available diphenylmethane diisocyanate (MDI) based isocyanates like MDI isomers, that is to say 4,4'-diphenyl-methane diisocyanate, 2,4'-diphenylmethane diisocyanate and mixtures thereof and polymeric MDI  
5 having an isocyanate functionality of more than 2. Whilst diisocyanates are the preferred polyisocyanates for use in the preparation of the polyisocyanate compositions, mixtures of diisocyanates with minor proportions of higher functionality polyisocyanates may be used if desired.

10 Other MDI variants are well known in the art and include liquid products obtained by the introduction of urethane, allophanate, urea, biuret, carbodiimide, uretonimine and/or isocyanurate residues.

The polyether polyols used for preparing the prepolymer contain up to 35% by weight  
15 ethylene oxide groups; at least 50%, and preferably at least 75% of these ethylene oxide groups are present at the end of the polyether polyol (tipped).

These polyether polyols have an average nominal functionality of 2-6, preferably of 2-4. They have a number average molecular weight of 1000-6000.

20

Polyether polyols which may be used for preparing the isocyanate-terminated prepolymer include products obtained by the polymerisation of ethylene oxide with another cyclic oxide, for example propylene oxide or tetrahydrofuran in the presence of polyfunctional initiators. Suitable initiator compounds contain a plurality of active hydrogen atoms and  
25 include water and polyols, for example ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, cyclohexane dimethanol, resorcinol, bisphenol A, glycerol, trimethylolpropane, 1,2,6-hexanetriol or pentaerythritol. Mixtures of initiators and/or cyclic oxides may be used.

30 Especially useful polyether polyols include poly(oxyethylene-oxypropylene) diols and triols obtained by the sequential addition of propylene and ethylene oxides to di- or trifunctional initiators as fully described in the prior art. Mixtures of the said diols and triols can be useful as well. Other useful polyether polyols include polytetramethylene



glycols obtained by the polymerisation of tetrahydrofuran. Polyester polyols may also be used for preparing the prepolymer.

The isocyanate-terminated prepolymer is prepared by reaction of an excessive amount of the polyisocyanate and the polyether polyol in order to obtain a prepolymer having the indicated NCO value. Methods to prepare prepolymers have been described in the art. The relative amounts of polyisocyanate and polyether polyol depend on their equivalent weights and on the desired NCO value and can be determined easily by those skilled in the art. If desired, the reaction may be conducted in the presence of catalysts which enhance the formation of urethane groups, like tertiary amines and tin compounds. In general the reaction time is between 30 minutes and 4 hours and the temperature between 50.degree. and 90.degree. C.

At least 90% of the groups obtained by reacting the polyisocyanate and the polyether polyol for preparing the prepolymer are polyurethane groups. To the prepolymers so prepared a polyisocyanate may be added provided the NCO value remains in the indicated range. The amount added in general is less than 25% by weight based on the total polyisocyanate composition. The added polyisocyanate may be selected from those mentioned above. Aromatic polyisocyanates and in particular MDI based polyisocyanates are preferred.

In accordance with another embodiment of the present invention, it has been found that the compound-intercalated phyllosilicate of the present invention can be co-intercalated easily with a co-intercalant polymer to form an intercalate that has unexpectedly superior intercalate dispersibility in a matrix polymer, and unexpectedly can be co-intercalated with higher amounts of co-intercalate polymer molecules. The intercalate also can be added to any other matrix polymer to enhance a number of properties of the matrix polymer, including modulus strength, heat distortion temperature, glass transition temperature, gas-impermeability, elongation, and the like.

"Matrix Polymer" shall mean a thermoplastic or thermosetting polymer that the Intercalate or Exfoliate is dispersed within.

The intercalates and co-intercalates of the present invention are easily, homogeneously and uniformly dispersed in a matrix polymer to provide improved properties to matrix polymers. The above and other aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention.

5

Layered clay :

Clay materials especially suitable for use within the particular invention are those which belong to the family of smectite clays such as montmorillonite, hectorite. These clay  
10 materials are known to be swellable with compatible compounds and therefore 'd' increases. More generally these clays are members of the family of 2:1 layered silicates. In this particular invention the preferred clays are montmorillonite clays. The clay platelet size is typically around 1nm thick and between 200-1000nm in diameter.

The preferred layered clays are modified clays which have been modified with onium ions  
15 comprising at least one long alkyl chain (>C8) and three other substituents. Presence of reactive functionality of at least one of the substituents with the constituents of the polymeric matrix is desired to achieve the enhanced properties. The long alkyl chain is desirable to promote intercalation by interaction with the hydrophobic unit of the compound and / or any constituents of the polymeric matrix, thus enabling de-lamination  
20 of the clay. Suitable clays are commercially available.

The amount of the clay which forms part of the nano dispersion is preferably less than 40wt%, more preferably less than 10wt%, and most preferably less than 6wt% clay by weight of the total nano dispersion.

25

Without insisting to be bound by theory it is believed that, upon mixing of the compound with the modified clay the gallery spacing 'd' between the layers of the clay further increases. This is the second expansion or swelling of the clay, the first expansion having already taken place by the modification of the layered clay. The mechanism is not properly  
30 known at this stage, however it is believed that there is an interaction between the long alkyl chain of the onium ion, which is hydrophobic and the hydrophobic unit of the compound and / or the constituents of the polymeric matrix. A further interaction of the hydrophilic units of the compound and the inner surfaces of the clay tactoids is believed.

These interactions may take the form of Van der Waals forces, hydrogen bonding and / or dipolar interactions.

5 The gallery spacing of the layered clay is typically less than 9Angstrom and that of the modified clay is typically less than 25A. The clay subsequent to the intercalation of the hydrophobic unit tipped with hydrophilic units swells to a new 'd' of greater than 40A and most preferably greater than 50A. The amount of swelling is a function of the compound.

10 The interlaminar spacing of adjacent layers (platelets) of the layered material (d-spacing minus one platelet thickness of the layered material) is expanded by contacting the layered material with the compound for subsequent intercalation with co-intercalant polymer reactants, an oligomer co-intercalant or a polymer co-intercalant, thereby leaving more space for co-intercalation of an oligomer or polymer when compared with a compound which is not intercalated. Therefore, polymerizable monomers capable of reacting to form  
15 a polymer co-intercalant, or polymerizable oligomer co-intercalant molecules, or a co-intercalant polymer can be easily and more fully intercalated between adjacent platelets of the layered silicate material, e.g., smectite clay platelets.

Intercalating compound :

20

The intercalating compound is characterized in that the compound contains one or more hydrophilic terminal groups (hereinafter referred to as intercalating compound)

25 Preferably the intercalating compound is characterized in having a hydrophobic unit (B) tipped with hydrophilic units (A).

The hydrophilic terminal group is preferably selected from the group consisting of monomers, oligomers or polymers of alkyleneoxide, ether, alcohol, vinylalcohol, pyrrolidone, acid, anhydride, ester, epoxy, amine oxide, sugars or mixtures thereof

30 Most preferably, said hydrophilic terminal groups contain oxyethylene units.

The hydrophobic unit is preferably selected from the group consisting of monomers, oligomers or polymers of alkyleneoxide, ether, ester, carbonate, styrene, olefin, siloxane, acrylate, oils or mixtures thereof.

Preferably the intercalating compound contains at least two hydrophilic terminal groups,  
5 more preferably said hydrophilic groups being identical.

Types of compounds which fit the description of the intercalating compound of the present invention including block or graft (branched chain) copolymers. These copolymers may be block or random in configuration. The hydrophilic units do not need to be identical.

10 By hydrophilic is meant if the monomer were homopolymerized, the polymer would be water soluble. A monomer which may not form a water-soluble homopolymer but which, in the amount used in a copolymer results in a water-soluble copolymer is also viewed in a broader sense within the definition of hydrophilic.

15 In a preferred embodiment of the present invention, the compound is a block copolymer, wherein the hydrophobic unit is chosen to be propyleneoxide and the hydrophilic unit is chosen to be ethylene oxide. The mole ratio of ethyleneoxide to propyleneoxide being within the range of 1:99 to 9:1 and most preferably 1:1 to 1:9

20 Examples of commercially available block copolymers are marketed under the trademarks of Daltocel by Huntsman, Pluronic by BASF-Wyandotte, Arcol and Acclaim by Lyondell, and Synperonic by Uniqema.

25 Preferred intercalating compounds of the present invention are polyols especially ethylene oxide-capped polyols. Ethylene oxide-capped polyols have long been valuable in the polyurethane industry because of the favorable reactivity of their primary hydroxyl groups with polyisocyanates. EO-capped polyols are normally made in two steps. First, propylene oxide (or a mixture of propylene oxide and ethylene oxide) is polymerized in the presence  
30 of a basic catalyst (usually potassium hydroxide) to produce a polyol that contains mostly or exclusively secondary hydroxyl groups. Second, ethylene oxide is added to the catalyst-containing mixture to convert some or most of the secondary hydroxyl groups to primary

hydroxyl groups. The process conveniently uses the same catalyst (usually KOH) for both the propoxylation and ethoxylation steps.

The ethylene oxide-capped polyols used have a number average molecular weight of 500 to 20000, preferably 2000-15000, and an average nominal functionality of 2-6, and may be selected from polyesters, polyesteramides, polythioethers, polycarbonates, polyacetals, polyolefins, polysiloxanes and polyethers. The polyester polyols have an average nominal functionality of 2-4, especially those having a number average molecular weight of 1000-10000 and an average nominal functionality of 2-3, and polyether polyols have an average nominal functionality of 2-6, preferably 2-4 and a number average molecular weight of 1000-20000, especially 2000-15000 and mixtures thereof.

Polyether polyols which may be used include products obtained by the polymerisation of a cyclic oxide, for example ethylene oxide, propylene oxide, butylene oxide or tetrahydrofuran in the presence, where necessary, of polyfunctional initiators. Suitable initiator compounds contain a plurality of active hydrogen atoms and include water, butanediol, ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, ethanolamine, diethanolamine, triethanolamine, toluene diamine, diethyl toluene diamine, phenyl diamine, diphenylmethane diamine, ethylene diamine, cyclohexane diamine, cyclohexane dimethanol, resorcinol, bisphenol A, glycerol, trimethylolpropane, 1,2,6-hexanetriol, pentaerythritol, sorbitol and sucrose. Mixtures of initiators and/or cyclic oxides may be used.

Especially useful polyether polyols include polyoxypropylene and poly(oxyethylene-oxypropylene) polyols obtained by the simultaneous or sequential addition of ethylene and propylene oxides to an initiator as fully described in the prior art.

The polyether polyols may be of the polymer polyol type, generally known in the art.

Polyester polyols which may be used include hydroxyl-terminated, reaction products of polyhydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, 1,4-butanediol, bis(hydroxyethyl) terephthalate, glycerol, trimethylolpropane, hexanediol, neopentyl glycol, methylpentane diol, pentaerythritol or

polyether polyols or mixtures of such polyhydric alcohols, and polycarboxylic acids, especially dicarboxylic acids or their ester-forming derivatives, for examples succinic, glutaric and adipic acids or their dimethyl esters, sebacic acid, phthalic anhydride, tetrachlorophthalic anhydride or dimethyl terephthalate or mixtures thereof.

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The nanodispersion may further comprise various optional components which are additives commonly employed with polar organic liquids. Such optional components include catalysts, nucleating agents, fillers, plasticizers, impact modifiers, chain extenders, plasticizers, colorants, mold release lubricants, antistatic agents, pigments, fire retardants, and the like. These optional components and appropriate amounts are well known to those skilled in the art.

10

Another embodiment of the present invention is directed to process for the production of nano composite materials of the present invention, whereby the intercalation/exfoliation is produced by mixing.

15

When shear is employed for exfoliation, any method which can be used to apply a shear to the intercalate/matrix polymer nanocomposite composition can be used. The shearing action can be provided by any appropriate method, as for example by mechanical means, by thermal shock, by pressure alteration, or by ultrasonics, all known in the art. In particularly useful procedures, the composition is sheared by mechanical methods in which the intercalate, with or without the carrier or solvent, is sheared by use of mechanical means, such as stirrers, Banbury® type mixers, Brabender® type mixers, long continuous mixers, and extruders. Another procedure employs thermal shock in which shearing is achieved by alternatively raising or lowering the temperature of the composition causing thermal expansions and resulting in internal stresses which cause the shear. In still other procedures, shear is achieved by sudden pressure changes in pressure alteration methods; by ultrasonic techniques in which cavitation or resonant vibrations which cause portions of the composition to vibrate or to be excited at different phases and thus subjected to shear. These methods of shearing are merely representative of useful methods, and any method known in the art for shearing intercalates may be used.

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In another embodiment, the present invention is directed to said nanodispersions further comprising an isocyanate reactive compound which optionally may be co-intercalated (as co-intercalant polymerizable reactants, or as the oligomer co-intercalant or polymer co-intercalant) to form nanocomposite materials. Preferred co-intercalants are polyols.

5

Suitable isocyanate-reactive monomer or oligomer or polymer to be used for the present invention include any of those known in the art for the preparation of polyurethanes. Of particular importance are polyols and polyol mixtures having average hydroxyl numbers of from 20 to 300, especially from 25 to 150 mg KOH/g, and hydroxyl functionalities of from 1.5 to 3, especially from 1.8 to 2.2, and a MW generally from 750 to 6000. Suitable polyols have been fully described in the prior art and include reaction products of alkylene oxides, for example ethylene oxide and/or propylene oxide, butylene oxide and tetrahydrofuran with initiators containing from 2 to 8 active hydrogen atoms per molecule. Other suitable polymeric polyols include polyesters obtained by the condensation of appropriate proportions of glycols and higher functionality polyols with dicarboxylic or polycarboxylic acids. Still further suitable polymeric polyols include hydroxyl terminated polythioethers, polyamides, polyesteramides, polycarbonates, polyacetals, polyolefins and polysiloxanes. The isocyanate-reactive compound is preferably a polyol which is preferably a polyether or a polyester or mixtures thereof. Mixtures may be used.

20

Polyamines likewise have an important role as components for preparing polyurethanes, in particular since they have higher reactivity than comparable polyols. As with the polyols, the polyamines used may be either low-molecular-weight polyamines, e.g. aliphatic or aromatic di- or polyamines, or polymeric polyamines, e.g. poly(oxyalkylene)polyamines.

25

Suitable poly(oxyalkylene)polyamines, which are obtainable, for example, from polyether polyols as given in U.S. Pat. No. 3,267,050, preferably have molecular weight of from 1000 to 4000 and are also obtainable commercially, e.g. under the designation JEFFAMINE®.

30

A chain extender is classically used; it is traditionally a low molecular weight polyol, typically a diol. The MW generally ranges from 62 to 750; the functionality generally ranges from 1.9 to 2.1. Examples of suitable diols include ethylene glycol, diethylene glycol, butanediol, triethylene glycol, tripropylene glycol, 2-hydroxyethyl-2'-hydroxypropylether, 1,2-propylene glycol, 1,3-propylene glycol, Pripol® (Uniquema,

35

Gouda, NL), dipropyl glycol, 1,2-, 1,3- and 1,4-butylene glycols, 1,5-pentane diol, bis-2-hydroxypropyl sulphide, bis-2-hydroxyalkyl carbonates, p-xylylene glycol, 4-hydroxymethyl-2,6-dimethyl phenol and 1,2-, 1,3- and 1,4-dihydroxy benzenes. PEG, PPG (e.g. 200) as well as PTHF (also known as PTMG) (e.g. 400) may also be used. Mixtures  
5 may be used.

The present invention is also directed to a reaction system for the process for production of nano composite materials, wherein said reaction system comprises a nano dispersion and a curing agent and optionally a chain extender, a viscosity modifier or de-gellant and a  
10 catalyst. The constituents of the reaction system are mixed together, wherein a co-intercalation of further reactants occurs within the gallery regions of the modified clay prior to curing of the polymeric matrix.

The term "reaction system" refers to a combination of ingredients wherein the  
15 polyisocyanate composition is kept in a container separate from the isocyanate-reactive ingredients

Low levels of a viscosity modifier or de-gellant (1-20wt% w/w clay) such as titanate or alkoxysilane may be added to reduce the viscosity of the nano dispersion and ease  
20 synthesis of the nano composite material. However, levels of this additive must be closely monitored to prevent loss of the nano dispersion. Low levels of this viscosity modifier have been shown to reduce the viscosity of the nano dispersion prior to curing without adversely effecting the nano composite formation and thus the inherent properties of the nano composite materials produced. However, higher levels of the viscosity modifier have  
25 been shown to reduce the amount of nano composite formation and therefore, the properties are adversely effected

The quantities of the polyisocyanate compositions and the polyfunctional isocyanate-reactive compositions as well as those of the chain extender to be reacted (in the absence of end-cap  
30 monomer) will depend upon the nature of the polyurethane to be produced and will be readily determined by those skilled in the art. The isocyanate index can vary within broad limits, such as between 70 and 400.



Molding compositions comprising a matrix polymer containing a desired loading of the co-intercalates of the present invention, and/or individual platelets obtained from exfoliation of the co-intercalates manufactured according to the present invention, are outstandingly suitable for the production of articles having valuable properties.

5

The nano composite materials produced by this process are typically of the type elastomers, thermoplastic polymers, and / or thermoset polymers. These three polymers may be in the form of a film, a foam (free rise or moulded), a sheet, a tube, an adhesive, a casting resin, a compression moulding, and / or a coating.

10

The amount of the clay which forms part of the nano composite material is preferably less than 15wt%, more preferably less than 10wt%, and most preferably less than 5wt% by weight of the total nano composite material. Thus the enhancement of the properties is realised with low levels of filler.

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The nano composite materials formulated by the present invention are preferably in an exfoliated state.

## Examples

### Example 1

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*Example 1 demonstrates that hydrophilic terminal groups of the intercalating compound are essential to generate intercalated nanodispersions.*

10 A pre-calculated amount of the organoclay Cloisite 30 (montmorillonite clay modified with tallowbis(hydroxyethyl)methylammonium ion; obtained from Southern Clay Products) was dispersed in a known amount of a chosen polyol by mixing under high shear at ambient temperature. The chosen polyols were polypropyleneglycols either with or without polyethylene oxide terminal groups.

15 The d-spacing of the organoclay was shown by Small Angle X-Ray Scattering (SAXS) (synchrotron source (ESRF, Grenoble) energy was 10 ke V and the wavelength of the X-rays was 1.238 Angstroms. The scan range was from 10.8Å to 209Å (i.e.  $q=0.58\text{\AA}^{-1}$  to  $q=0.03^{-1}$ ) to be 18Å. SAXS analysis demonstrated that no intercalation of the clay galleries occurred with polypropylene glycol homopolymers (MW range 2000-6000).  
20 However, polyols consisting of a polypropylene glycol block with polyethylene oxide terminal groups intercalated the clay, as evidenced by an increase in gallery spacing from 18Å to >50Å. Furthermore, the observed d-spacing of the polyol/clay intercalate in the latter case was shown to be a function of the polyol MW and composition. In particular, an increase in d-spacing was observed with increasing molecular weight.

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### Example 2

*Example 2 demonstrates the enhanced properties that can be obtained in PU elastomers by nanodispersion of the organoclay.*

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A nanodispersion of the organoclay Cloisite 30 (3.6wt%) in an EO/PO polyol having a nominal functionality of 3, glycerol as initiator, hydroxyl value of 27mg/gKOH and an EO

content of 15wt% (all tipped) was prepared by mixing the constituents under high shear at ambient temperature. SAXS analysis confirmed intercalation of the clay galleries by the polyol with a d-spacing of 85Å. Subsequently, the polyol/clay nanodispersion was cured with 2-methyl-1,3-propanediol (chain extender), "Suprasec 3050" (50% mixture of 2,4'- and 4,4'-MDI), and Dabco S (catalyst from Air Products, DABCO is a trademark) to give  
5 solid a polyurethane thermoset elastomer (30% hard block) incorporating 2.5wt% nanodisperse organoclay.

Elastic Modulus at room temperature was measured using Dynamic Mechanical Thermal  
10 Analysis (DMTA) in flexural mode on specimens of dimensions 4cm x 1cm x 3.5 mm. A heating rate of 2°C min over a temperature range from - 100 to 200°C, frequency was 10 HZ and the applied strain was 4%.

Tensile strength and 100% secant modulus were measured at ambient temperature and a  
15 cross-head speed of 200mm/min on tensile specimens of type S2 (norm DIN53504; 3.5 mm thickness).

Shore A Hardness was measured according to standard DIN53505 on disc specimens of  
thickness 6mm or greater.

20 The nanocomposite material showed a much higher elastic modulus (3X), 100% secant tensile modulus (4X), tensile strength (3X) and Shore A Hardness (1.5X) compared to a reference elastomer prepared under identical conditions. It was equally shown that similar property enhancements were not achieved upon incorporation of 2.5-10wt% of  
25 microdisperse fillers such as sodium montmorillonite, fine grade talc (Luzenac Steamic OOS; PS50=1.6micron), calcium carbonate and barium sulphate.

### Example 3

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*Example 3 demonstrates the properties of thermoplastic polyurethane nanocomposites,*

Nanodispersions of pre-calculated amounts of the organoclay Cloisite 30 in a mixture of butanediol (chain extender) and an EO/PO polyol having a nominal functionality of 2, hydroxyl value of 28mg/gKOH and EO content of 15wt% (all tipped) were prepared by mixing the constituents under high shear at ambient temperature. Thermoplastic polyurethane nanocomposite elastomers incorporating 2.5wt% nanodisperse organoclay were prepared by curing these nanodispersions with isocyanate chosen from "Suprasec 3050" (50% mixture of 2,4'- and 4,4'-MDI), "Suprasec® 3030" (30%/70% mixture of 2,4'- and 4,4'-MDI) and "Suprasec® 2433" (prepolymer of 4,4-MDI, with a uretonimine content of 2.7wt%, with an EO/PO polyol having a nominal functionality of 2, a hydroxyl value of 30mg/gKOH, and an EO content of 15wt% (all tipped); isocyanate value 19%) in the presence of the catalyst DABCO® S.

SAXS analysis of each of the nanocomposites materials showed no peaks, indicating that the clay was in an exfoliated state.

15

The ambient temperature elastic modulus, 100% secant tensile modulus and tensile strength were measured according to the procedures detailed in example 2. Abrasion Resistance was determined on specimens of 16mm diameter and at least 7 mm thickness according to DIN53516.

20

The melt viscosities of the TPUs were measured by capillary rheometry after pre-drying of the materials at 80°C for 16 hours. The measurements were made using a Rosand Rh-2000 capillary rheometer by extruding the polymer through a single bore barrel of diameter 16 mm and length 180 mm fitted with 1 mm diameter dies. Isothermal experiments were carried out at a selected melt temperature using a shear rate sweep from 50s<sup>-1</sup> to 4600s<sup>-1</sup>.

25

Increases in the ambient temperature elastic modulus (1.5-3X), 100% secant tensile modulus (1.6-2.7X) and tensile strength (1.2-3.5X) and Shore A Hardness (1.05-1.5X) were observed for all of the nanocomposite materials compared to reference formulations. Abrasion resistance was also improved by a factor of 35-50% for the nanocomposite materials compared to the reference materials. An increase in high temperature softening point of typically 10-25°C was observed for the nanocomposites with respect to the reference systems. The nanocomposite materials displayed characteristic TPU melt

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behaviour but with higher melting temperatures and a greater degree of shear-thinning than the reference materials.

Increased thermal and thermo-oxidative stability of the thermoplastic polyurethane nanocomposites relative to reference materials was demonstrated by thermogravimetric analysis under nitrogen and air. In addition, the nanocomposite materials showed intumescent fire behaviour and much lower heat release than reference materials in cone calorimetry experiments.

10

#### **Example 4**

*The following example illustrates the utility of an organotitanate processing aid in reducing the viscosity of polyol/organoclay nanodispersions and also the importance of titrating the levels of organotitanate to avoid loss of nanodispersion.*

15

Nanodispersions of Cloisite 30 (3.6wt%) in an EO/PO polyol having a nominal functionality of 3, glycerol as initiator, hydroxyl value of 27mg/gKOH and an EO content of 15wt% (all tipped) were prepared as described in example 2 with the exception that systematically increasing levels (0-0.35wt%) of the organotitanate "Kenreact Lica 12" (obtained from Kenrich Petrochemicals Inc) were added to the polyol prior to blending with the organoclay. It was observed that lower addition levels of the Kenreact Lica 12 (<0.03wt%) gave large reductions in viscosity, and thus better processability, whilst retaining 100% nanodispersion efficiency. However, higher levels of the same additive led to loss of the clay nanodispersion.

25

#### **Example 5**

*Example 5 describes the preparation of foamed polyurethane nanocomposite materials and the properties which are achieved.*

30

Nanodispersions of Cloisite 30 (3.6wt%) in an EO/PO polyol having a nominal functionality of 3, glycerol as initiator, hydroxyl value of 28mg/gKOH and an EO content of 15wt% (all tipped) were prepared as described in Example 2. Free-rise foams of approximately 400kg/m<sup>3</sup> density (30% hard block; 2.5wt% nanodisperse organoclay) were synthesised by curing the nanodispersions with monoethylene glycol (chain extender), water and Suprasec 3050 (50/50 mixture of 2,4'' and 4,4''MDI) in the presence of DABCO EG catalyst (catalyst from Air Products, DABCO is a trademark).

Elastic modulus at room temperature was measured Dynamic Mechanical Thermal Analysis (DMTA) in bending mode on specimens of dimensions 4cm x 1cm x 3.5mm. The test frequency was 1Hz and a heating rate of 3°C/min over a temperature range from -100 to 200° was employed.

Tensile strength and E-modulus were measured at ambient temperature and a cross-head speed of 100 mm/min on tensile specimens of type S1 (modified DIN53504 method; 4 mm thickness).

Compression hardness and hysteresis were measured at ambient temperature. Specimens of dimensions 2.5cm x 2.5cm x 1cm were indented for 4 cycles at a speed of 100mm/minute to 75% of the original thickness. Stresses at 40% (CLD40) , 50% (CLD 50) and 65% (CLD 65) compression and hysteresis loss were calculated from the fourth cycle (modified DIN53577 method)

SAXS analysis of the foams demonstrated that the clay was in an exfoliated state. Significant increases in elastic modulus (3X), 100% secant tensile modulus (2X), tensile strength (>2X) and compression hardness (e.g. 1.6X increase in CLD40) were observed without any increase in hysteresis loss under compression cycling.

### Example 6

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*Example 6 demonstrates the properties and melt behaviour of thermoplastic polyurethane nanocomposites prepared using the compound and a co-intercalating polyol.*

A pre-calculated amount of the organoclay Cloisite 30B was dispersed in a known amount of Terathane 2000 (polytetrahydrofuran with a nominal functionality of 2 and an hydroxyl value of 56.1 mgKOH/g; pre-heated to 50°C ) or Daltorez P765 (aliphatic polyadipate ester with a functionality of 2 and a hydroxyl value of 50mgKOH/g; pre-heated to 50°C) and a compound consisting of an EO/PO polyol having a nominal functionality of 2, an EO content of 15-40% by weight (all tipped) and an hydroxyl value of 10-22mgKOH/g by mixing under high shear at ambient temperature. SAXS analysis of selected dispersions showed that the organoclay was intercalated, with the d-spacing controlled by the compound.

10

The nanodispersions were cured with monoethylene glycol/butanediol (chain extenders) and "Suprasec 3030" (30%/70% mixture of 2,4'- and 4,4'-MDI) in the presence of DABCO S catalyst to form thermoplastic polyurethane nanocomposites. Elastic modulus at room temperature was measured using Dynamic Mechanical Thermal Analysis (DMTA) in flexural mode on specimens of dimensions 4cm x 1cm x 3.5mm. Heating rate of 2°C/min over a temperature range from -100 to 200°C, frequency was 10Hz and the applied strain was 4%.

15

Shore A Hardness was measured according to standard DIN53505 on disc specimens of thickness 6mm or greater.

20

In comparison to reference materials, the nanocomposites incorporating the polytetrahydrofuran polyol displayed increases in elastic modulus (2X), Shore A Hardness (1.2X) and softening point (10-25°C) whilst the analogous nanocomposite incorporating the polyester polyol exhibited an increased softening point(10-25°C) . The nanocomposite materials displayed characteristic TPU melt behaviour but with higher melting points than the reference materials.

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## Claims

1. A nano dispersion comprising a layered clay and a compound intercalated within the gallery regions of said clay, characterised in that said compound contains one or more hydrophilic terminal groups.  
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2. A nano dispersion according to claim 1, wherein said hydrophilic terminal group is selected from the group consisting of monomers, oligomers or polymers of alkyleneoxide, ether, alcohol, vinylalcohol, pyrrolidone, acid, anhydride, ester, epoxy, amine oxide, sugars or mixtures thereof  
10
3. A nanodispersion according to claims 1-2 wherein said hydrophilic terminal groups contain one ore more oxyethylene units.
- 15 4. A nanodispersion according to claims 1-3 wherein said compound contains a hydrophobic unit selected from the group consisting of monomers, oligomers or polymers of alkyleneoxide, ether, ester, carbonate, styrene, olefin, siloxane, acrylate, oils or mixtures thereof.
- 20 5. A nano dispersion according to claim 1, wherein said compound is a block or graft copolymer.
6. A nanodispersion according to claims 1-5, wherein said compound contains at least two hydrophilic terminal groups.  
25
7. A nanodispersion according to claim 6 wherein said hydrophilic groups are identical.
8. A nanodispersion according to claims 1-7, wherein the hydrophilic group is ethyleneoxide and the hydrophobic unit is propyleneoxide, the mole ratio of ethyleneoxide to propyleneoxide being within the range of 1:99 to 9:1 and more preferably 1:9 to 1:1.  
30
9. A nano dispersion according to claim 1, wherein the clay comprises:



less than 40wt%, more preferably less than 10wt%, and most preferably less than 6wt% by weight of the total nano dispersion composition.

5 10. A nanodispersion according to claims 1 to 9, wherein said clay being pre-modified with onium ions.

11. A nanodispersion according to claim 10 wherein said onium ions comprise:

- (i.) at least one alkyl group of greater than eight carbon chains (>C8)
- (ii.) at least one isocyanate reactive group.

10

12. A nanodispersion according to claims 1-11, further comprising an isocyanate reactive compound preferably selected from the group of polyols, polyamines or mixtures thereof.

15 13. A nano dispersion according to claim 12, whereby said isocyanate reactive compound is co-intercalated within the gallery regions of the clay

14. A reaction system comprising:

- (i.) a nano dispersion according to claims 1-13
- 20 (ii.) a curing agent, preferably a polyisocyanate

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15. A nano composite material produced by the reaction system according to claim 14, wherein optionally a chain extender, a catalyst and a viscosity modifier are co-intercalated within the gallery regions of the clay.

16. The nano composite material according to claims 15, wherein said nano composite material forms part of a polymeric matrix.

17. The nano composite material according to claims 15 and 16, wherein said nano  
30 composite material is an elastomer, a thermoplastic polymer, and / or thermoset polymer.

18. The nano composite material according to claims 15-17, wherein said nano composite material is a polyurethane.
19. The nano composite material according to claims 15-18, wherein the nano composite material is in an exfoliated state.  
5
20. A nano dispersion according to claim 1-13, wherein said intercalation is produced by mixing.
- 10 21. A nano composite material according to claim 15-18, wherein said intercalation is produced by mixing.